Synopsis

"A study of structural dynamics in polymer systems using dielectric spectroscopy"

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1. Introduction:

In the present days, the human civilization is most focussed term and the role of materials is the crucial one for the same. Hence people are much interested in material science. An important goal of researchers in material sciences is to synthesize and study different kinds of materials among which the polymers cover a vast range.

Polymer are natural or synthetic substances composed of very large molecules, called macromolecules, that are multiples of simpler chemical units called monomers. Polymers are classified as natural and synthetic. Due to their broad spectrum of properties, both synthetic and natural polymers play essential and ubiquitous role in everyday life [1]. Polymers make many of the materials in living organisms and is the basis of many materials and man-made materials. The polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins which are fundamental to all of the biological structure and their functioning. Both natural and synthetic polymers are produced via polymerisation of small molecules called monomers.

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exists in countless forms and numbers because of a very large number and types of atoms present in their molecules. Polymers can have different chemical structures, physical properties, mechanical behaviour, thermal characteristics etc. These can be classified as: natural polymers and synthetic polymers which are isolated from natural materials are called natural polymers [2] e.g. cotton, silk etc. The polymers which are synthesised from low molecular weight compounds are called synthetic polymers e.g. Polyethylene, PVC, nylon and terylene. A polymer whose back bone chain is essentially made of carbon atoms is termed as an organic polymer. The majority of synthetic polymers are organic and are very extensively studied. Some polymers soften on heating and can be converted into any shape that they can return on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Such polymers that soften on heating and stiffen on cooling such polymers are called thermoplastics. Thermosetting polymers are the polymers that become an infusible and insoluble mass on heating. They are like the yolk of egg which on heating sets into a mass and it cannot be shaped further. The polymers when vulcanised into rubbery

products exhibiting good strength and elongation are elastomers e.g. natural rubber, synthetic rubber, silicon rubber. Polymers used as adhesives, potting compound, sealants etc in liquid form are described as liquid resins [3].

By considering all these aspects, the polymer systems are selected for the present work by means of dielectric spectroscopy.

2. Review of literature:

The literature survey reveals that various liquid polymers such as Polyethylene Glycol-Lithium Trifluro Methane Sulphonate (PEG-LTMS) [04], Acetophenone [05], Polymer electrolytes [6,7], Polydimethyl siloxane (PDMS) [8], Polyvinylidene Fluoride (PVDF) [9], polymer based nanofluids [10] and many polymer solutions [11] are studied and solid polymers like polyvinyl acetate, gold nanoparticle doped polymer, polycaprolactone, PVP, optical polymer and polymer nanocomposite films [12-18] are also have been studied through dielectric measurements. Their dielectric parameters like dielectric constant, dielectric losses are obtained at different frequencies and at different temperatures. The ac conductivity behaviour of some polymers like Polypyrrole, Polyvinylidene Fluoride (PVDF), Nylon 6 [19-21] have been carried out which revealed the conductivity properties of polymers.

The broad-band dielectric relaxation measurements were performed for the four pentitols such as isomers, xylitol, adonitol, L&D-arbitol [22] and polymer electrolyte with the effect of adding amino acid are done for various frequencies and temperature through an ac dielectric analysis [23].

The dielectric spectroscopy of dielectric materials can be performed by applying frequency domain and time domain techniques. In TDR (Time Domain Reflectometry) technique, a train of fast rising pulses is applied to a sample through a co-axial line. This method at very high frequency range was first developed by H Fellner-Feldegg [24]. S. Mashimo et. al. [25] developed a TDR technique to find complex permittivity of aqueous solutions.

At present, the largely contributing scientists in this research field are D Bertolini [26], Y. Feldman [27-29], Udo Kaatze [29-32], S. C. Mehrotra [33-35], R. J. Sengwa [36-39], V. A. Rana [40, 41], A. C. Kumbharkhane [42-47] etc.

3. Objectives of research the hypothesis:

- To measure the complex permittivity of chosen polymers precisely.
- To evaluate electrical properties and dielectric properties such as static dielectric permitivity, relaxation time and high frequency dielectric permittivity.
- To study the molecular interactions in the polymer systems using Kirkwood correlation factor and Thermodynamic parameters.
- To find the Refractive Index of associated liquid polymers very precisely using abbe's refractometer.

4. Methodology to be adopted:

Time Domain Reflectometry (TDR) technique is very much useful for the measurement of complex permittivity spectra. A fast-rising voltage pulse with repetition frequency of few KHz and rise time of picoseconds is allowed to transmit through a coaxial line with characteristic impedance 50 Ohm. The co-axial cable with semi rigid copper and with flat end can be used. Sampling oscilloscope monitors changes in the pulse after reflection from the end of the line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were digitized with suitable sampling points in the selected time window. Mismatch in the impendence of these reflected pulses will be used to extract the complex permittivity spectra of liquid under test through data analysis.

The low frequency dielectric measurement can be done using precision LCR meter by applying frequency domain technique in the frequency range of few Hz to some MHz. In this technique, the capacitance and parallel resistance of the liquid dielectric test fixture without and with samples are measured.

5. Importance of study:

The following scientists are doing research in this field at national and international level:

International Status:

1. N Shiyanshiki, University of Tokyo, Tokyo, Japan
2. S Yagihara, University of Tokyo, Tokyo, Japan
3. S Sudo, Dept. of Physics, Tokyo City Univ. Tamazutsumi, Setagaya, Tokyo, Japan
4. A Katldo, Universita di Lecce, via Monteroni, 73100 Lecce, Italy
5. Udo Kaatze, DrittesPhysikalischesInstitut Georg-August-Universitat Gottingen, Germany.
6. Yuri D Feldman, Department of Applied Physics, Hebrew University of Jerusalem, Jerusalem, Israel.

National Status:

1. S. C. Mehrotra, Dr. BAMU, Aurangabad, Maharashtra
2. R. J. Sengwa, JNV University, Jodhpur, Rajasthan
3. A. C. Kumbharkhane, SRTM University, Nanded, Maharashtra
4. V. A. Rana, Gujrat Univirsity, Ahmedabad, Gujrat

Significance and society applications of the study:

Polymer are essential material that widely used in a lot of product used in daily life and it is unimaginable to live without them. Their dielectric relaxation studies reveals many of the important characteristics of the polymer materials. These results and observations obtained through the dielectric study can be used to develop and examine many polymer materials and enhance their applicability.

6. Work plan/ formulation and structure of study:

- **First Year:** To study theoretical background of research problem and detail literature survey. The dielectric measurement of polymers in liquid form in different frequency ranges.

- **Second Year:** Evaluate the dielectric parameters such as static dielectric permitivity, relaxation time, high frequency dielectric permittivity using experimental data. To study the effect of temperature and aging on the dielectric properties of these materials.

- **Third Year:** To discuss the results obtained from the dielectric data. To publish the work in research journals of repute and presenting the work in conference/seminars. Finally, write up the research work for doctoral thesis.

References:

1. N. G. McCrum, C. P. Buckley, C. B. Bucknall (1997). Principles of polymer engineering. Oxford; New York: Oxford University Press. p. 1. ISBN 978-0-19-856526-0.
2. V. R. Gowarikar, N. V. Vishwanathan, J. Sreedhar, (1988) Book: polymer science, New York, ISBN 0-470-20322-6.
3. M. G. Arora, M. Singh (2002) Book: Polymer Chemistry.
4. R. V. Patil, D. Praveen , R. Damle, IOP Conference Series, Materials Science and Engineering, 310 (2018) 012120.
5. Y. Yomogida, R. Nozaki, Journal of Molecular Liquids 149 (2009) 101–104.
6. A. Chandra, A. Chandraa, K. Thakur, ISSN 1070-3632, Russian Journal of General Chemistry (2013) Vol. 83, No. 12, pp. 2375–2379.
7. H. Nithya, S. Selvasekarapandian, D. Arun Kumar, A. Sakunthala, M. Hema, P. Christopherselvin, J. Kawamura, R. Baskaran, C. Sanjeeviraja (2011) 126(1-2), 404–408.
8. M. Sangeetha, A. Mallikarjun, Y. Aparna, M. V. Reddy, J. S. Kumar, T. Sreekanth & M. J. Reddy (2021). Materials Today: Proceedings, 44, 2168–2172.
9. V. Samulionis, J. Macutkevic, J. Banys, J. Belovickis, O. Shenderova (2015). IOP Conference Series: Materials Science and Engineering, 87(), 012010.
10. G. T. Jinklor, J. P. Bokare, T. P. Kulkarni, M. S. Thane, S. S. Pachore, K. B. Kabara, A. V. Sarode(2019). AIP Conference Proceedings 2142(), 200005.

11. H. Nakamura, S. Mashimo and A. Wada, Japanese Journal of Applied Physics, Vol. 21, No. 3, March, 1982 pp. 467-474.
12. J. K. Hartt and E. F. Carr., The Journal of Chemical Physics 36, 2523 (1962).
13. D. Jayoti and P. Malik, AIP Conference Proceedings 1953, 100085 (2018).
14. J. I. Chen , R. A. Moody, Y. M. Chen, J. Y. Lee, S. K. Sengupta, J. Kumar, and S. K. Tripathy, Vol. 247, Materials Research Society(1992).
15. M. Sadiq, A. Arya and A. L. Sharma, Springer International Publishing Switzerland (2017) V.K. Jain et al. (eds.), Recent Trends in Materials and Devices, Springer Proceedings in Physics 178.
16. V. J. Hegde, O. Gallot-Lavallee, 978-1-5090-2804-7/16/$31.00 (2016) IEEE.
17. B. R. Kumar, S. K. Shahenoor Basha, & M. C. Rao, AIP Conference Procedding 1953, 100002-1–100002-4 (2018).
18. M. S. Kumar, M. C. Rao, Materials Today: Proceedings 5 (2018) 26405–26410.
19. A. Sunilkumar, S. Manjunatha, Y. T. Ravikiran, M. Revanasiddappa, M. Prashantkumar, T. Machappa, Polymer Bulletin(2021).
20. C. Patel, N. Thankachen, P. Sengunthar, S. Patel & U. S. Joshi (2021). Materials Today Proceedings, 47, 668–671.
21. K. Sreelatha and P. Predeep Proceeding of International Conference on Recent Trends in Applied Physics and Material Science AIP Conference Procedding 1536, 477-478 (2013).
22. L. Carpentier, M. Paluch, S. Pawlus (2011), The Journal of Physical Chemistry B, 115(5), 1062–1066.
23. K. Sundaramahalingam, S. Jayanthi, D. Vanitha & N. Nallamuthu (2021). Ionics, 27(9), 3919–3932.
24. H. Fellner-Feldegg, Journal of Physical Chemistry 73, 616, (1969).
25. S. Mashimo, T. Umehara, T. Ota, S. Kuwabara, N. Shinyashiki, S. Yagihara, Journal of Molecular Liquids 36, 135 (1987).
26. V. Raicu, Y. D. Feldman, Book- Dielectric Relaxation in Biological Systems Physical Principles, Methods and Applications, ISBN: 978–0–19–968651–3.
27. Y. D. Feldman, A. Punzenko, P. B. Ishai, Physical Review Letter, 105.037601, PRL 105, 037601 (2010).
28. Y. D. Feldman, I. Popov, P. B. Ishai, A. Khamzin, Physical Chemistry Chemical Physics, 18 (20) (2016) pp. 13941-13953.

29. L. Latypova, A. Puzenko, A. Bogdanova, Y.D. Feldman, 13th International Conference on Electromagnetic Wave Interaction with Water and Moist Substances (ISEMA)-2021.
30. U. Kaatze, Y. D. Feldman, Measurement Science And Technology, 17 (2006) R17–R35.
31. U. Kaatze, Journal of Molecular Liquids 315 (2020) 113788.
32. U. Kaatze, "Water: Why Is it So Special?", IEEE2018.
33. S. C. Mehrotra, R. J. Sengwa, R. Chaudhary, Molecular Physics, 99 (21) (2001) 1805-1812.
34. S. C. Mehrotra, V. A. Rana, A. D. Vyas, Journal of Molecular Liquids 102/1–3 (2002) 379–391.
35. B. G. Lone, S. C. Mehrotra, P. B. Undre, S. S. Patil, P. W. Khirade, Journal of Molecular Liquids 141, 47–53(2008).
36. R. J. Sengwa, Journal of Molecular Liquids, 108(1-3) (2003) 47–60.
37. R. J. Sengwa, S. Sankhla, N. Shinyashiki, Journal Solution Chemistry, 37: 137–153 (2008).
38. R. J. Sengwa, S. Choudhary, P. Dhatarwal, (2017), Journal of Molecular Liquids, 225, 42–49.
39. S. Choudhary, P. Dhatarwal, R. J. Sengwa (2017) Journal of Molecular Liquids, 231(), 491–498.
40. V. A. Rana, V. A. Pandit,. Journal of Molecular Liquids, (2020), 113673.
41. N. S. Shah, P. S. Shah, V. A. Rana, Ionics 21(12) (2015) 3217–3222.
42. S. S. Kadam, K. S. Kanse, Y. S. Joshi, D. N. Rander, , A. C. Kumbharkhane, Indian Journal Physics (2018).
43. A. Mohan, M. Malathi, S. S Shaikh, A. C. Kumbharkhane, Journal of Solution Chemistry, 45(2), 221–234 (2016).
44. D. N. Rander, Y. S. Joshi, K. S. Kanse, A. C. Kumbharkhane, Indian Journal of Physics, 90(1), 67–72 (2016).
45. D.G. rathod, D.N. Rander, K.S. Kanse, Y.S. Joshi, A.C. Kumbharkhane, Journal of the Maharaja Sayajirao University of Baroda, ISSN: 0025-0422, Volumr-55, No.2 (2021).
46. D. G. Rathod, D. N. Rander, K. S. Kanse, Y. S. Joshi, A. C. Kumbharkhane, Carbohydrate Research 507 (2021) 108375.

47. P. A. Bhadane, D. N. Rander, K. S. Kanse, Y. S. Joshi, A. C. Kumbharkhane, Physics and Chemistry of Liquids(2020) 1-9.

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